1903
K96

KUTSCH

Separation of Tin, Arsenic, & Antimony

Chemistry
B. S.
1903

UNIVERSITY
OF
ILL. LIBRARY

UNIVERSITY OF ILLINOIS
LIBRARY

Class 1903 Book K96 Volume

Je 05-10M

A New Method for the Separation of Tin, Arsenic and Antimony with Special Reference to Complex Alloys

BY

WILLIAM A. KUTSCH

THESIS

FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

COLLEGE OF SCIENCE

UNIVERSITY OF ILLINOIS

PRESENTED JUNE 1903

1903
K96
gNo5 Ridder

A NEW METHOD FOR THE SEPARATION AND DETERMINATION OF TIN, ARSENIC AND ANTIMONY WITH SPECIAL REFERENCE TO COMPLEX ALLOYS.

The term alloy, in its most general acceptation means the mutual combination of two or more metals. The earliest historical data in reference to the development of the art of preparing alloys are very meager and though it appears from passages in history that no metallic compound was in more general use than brass, the mode of its manufacture is left in obscurity. The Greeks possessed considerable knowledge in the art of mixing metals and knew how to prepare alloys with special properties which rendered them suitable for particular purposes. There can scarcely be any doubt that the alloys of copper with tin generally called bronzes were the earliest mixtures of metals, because zinc, in a metallic state has only been known at a later period, while tin was known in the earliest historic times. Next in historical order follow the alloys of the noble metals with each other and with copper. Up to the commencement of the reign of Charlemagne when the development of technical arts commenced in Europe the only mixtures of metals were alloys of copper, tin, zinc, silver and gold, and some amalgams. To prepare other alloys a greater knowledge of chemistry was required than that possessed by the early races of mankind. The art of preparing alloys, however, became only a branch of chemistry when the latter somewhat more than a century ago entered the ranks of the sciences. The chemists gradually

UIUC

investigated all the bodies occuring in nature and showed how from the minerals a series of metals could be gained, which were not known up to that time. These metals were examined in regard to their intrinsic properties which made them suitable for technical purposes.

At the present time the manufacture of alloys is very extensive and tin and antimony are not only the chief constituents of various alloys, but form an important factor in other alloys. Copper and zinc can be mixed together within very wide limits to form the brasses. Copper and tin are alloyed to form bronzes, gun metals and bell metals. Alloys in which tin is the chief constituent are chiefly used for bearings and are commonly called Babbit metals. The metal originally consisted of 1 part of copper, 2 of antimony, and 6 of tin, but at present these constituents vary within wide limits and lead, iron, and zinc are also used. Britannia metal is a tin and antimony alloy. Lead is alloyed with antimony to form typemetals, and with arsenic to form shot metals. Perhaps the most important class of alloys is the bearing metals. Experience has shown that alloys of definite composition are best suited to certain purposes,and it has therefore become necessary to accurately determine the constituents of these metals. Various methods have been proposed for the analysis, the most practicable of which are the following.

Clarke's method (1) consists in treating hydrochloric acid solution of tin arsenic and antimony with oxalic acid, the antimony and arsenic being precipitated after thoroughly saturating the solution with H_2S. The filtrate is made alkaline with ammonium hydroxide and the precipitated tin sulphide dissolved in yellow

Digitized by the Internet Archive
in 2013

http://archive.org/details/newmethodforsepa00kuts

ammonium sulphide. An excess of acetic acid precipitates the tin as the oxide.

Garnot's method (2) for the separation of tin and antimony consists in treating a hydrochloric acid solution of these metals with oxalic acid to keep back the tin. Sodium thio-sulphate precipitates the antimony from this solution as the sulphides.

Drown's method consists in the volatilization of the chloride of tin, arsenic and antimony and their absorption in a solution of potassium bromide. Arsenic is distilled from the potassium bromide solution and the tin and antimony separated according to Garnot's method.

Berglund's method (3) consists in boiling a solution of the sulphides of tin arsenic and antimony in sodium sulphide, with copper oxide. The cuprous sulphide which formed is removed by filtration and the antimony separated by the addition of alcohol.

✓ Bunsen's method (4) consists in dissolving the sulphides of arsenic and antimony in a solution of potassium hydroxide and volatilizing the arsenic by means of chlorine gas.

✓ Kassner's method (5) consists in dissolving the sulphides of tin and antimony in sodium peroxide and acidifying the solution. After long boiling tin oxide is precipitated and the antimony in the filtrate is precipitated with alcohol.

Hampe (6) dissolves the sulphides of tin arsenic and antimony in hydrochloric acid and oxidizes with potassium chlorate. Tartaric acid is added and the solution made alkaline with ammonium hydroxide. The arsenic is precipitated with magnesia mixture, and the tin and antimony in the filtrate with hydrogen sulphide. The sulphides are dissolved in sodium peroxide and the antimony

precipitated as sodium antimonate with alcohol. If antimony is present in larger amount than the tin and arsenic it may be separated first by extracting the mixed sulphides with sodium sulphide and oxidizing with sodium peroxide. Alcohol precipitates the antimony from this solution but the presence of a large amount of sodium salts prevents the precipitation of the arsenic in the filtrate with magnesia mixture. The alcohol is driven off and the solution acidified with hydrochloric acid in order that the arsenic and tin may be precipitated as sulphides and separated in the usual manner.

Warren (7) dissolves the sulphides in aqua regia evaporates to a small bulk to remove the nitric acid and precipitates the tin with potassium ferrocyanide. The precipitate of stannic ferrocyanide is dried, reduced with hydrogen in a crucible with a tubular lid, dissolved in hydrochloric acid and precipitated as the sulphide.

Marburg (8) has devised a method of separation from the fact that arsenic and antimony sulphides are soluble in lime water, and tin sulphide is insoluble.

Lang, Carson and Mackintosh (9) treat the sulphides of tin arsenic and antimony with concentrated nitric acid and bring to dryness. The residue is extracted with water and the arsenic in the solution determined by magnesia mixture. The residue is digested with tartaric acid which extracts all the antimony leaving the tin as tin oxide.

Herroun's method (10) for the volumetric determination of antimony in the presence of tin depends on the fact that antimony tetrachloride is reduced to the di-chloride by hydrochloric acid in the presence of tin tetrachloride.

Weil's method (11) depends upon the reduction of antimonic

and cupric chlorides by stannous chloride. The antimonic and antimonous chlorides are both soluble and colorless, but the solution of the former is given a greenish-yellow coloration by the addition of a cupric chloride solution. A given volume of standard copper solution is added to the antimonic solution and from the volume of standard stannous chloride solution required to decolorize, the amount of antimony is calculated.

Causse (12) describes a volumetric method for the estimation of antimony, which is based on the fact that when antimonic acid, either free or combined comes into the presence of iodic acid, this acid is destroyed and a quantity of iodine proportional to the amount of iodic acid decomposed is set free.

$$5Sb_2O_3 + 2IO_5 = Sb_2O_5 + 2I_2.$$

Reuter (13) precipitates antimony as sulphide in excess of axalic acid to keep back the tin, dissolves the sulphide in concentrated hydrochloric acid and titrates with potassium permanganate.

$$5SbCI_3 + 16HCl + 2KMnO_4 = SbCl_5 + 2KCl + 2MnCl_2 + 8H_2O.$$

Weller's (14) method for the separation of tin from antimony is based on the fact that in an acid solution of antimonic pentachloride and stannic chloride, only the antimony is reduced by potassium iodide. The hydrochloric acid solution of tin and antimony is oxidized with potassium chlorate and a solution of potassium iodide is added. The liberated iodine is distilled into a potassium iodide solution and this solution titrated with sulphorous acid.

In the above methods yellow ammonium sulphide is used for the separation of tin, arsenic and antimony from the other members

of the group. According to the analyst (15) 5.71% of the total copper is soluble in yellow ammonium sulphide. It has also been shown that bismuth sulphide is soluble to a great extent in yellow ammonium sulphide.

The length of time and inaccuracies involved in the separation by means of yellow ammonium sulphide, and the elaborate apparatus needed for further separation by distillation methods, make such methods unsatisfactory for technical work.

Hagedorn (20) experimented upon the use of KOH instead of yellow ammonium sulphide. Different strengths of KOH solution were tried on the various sulphides and it was found that arsenic, antimony and stannic sulphides dissolved easily in a 2% solution, but the tin was precipitated on boiling. With a 1% solution of KOH tin was also precipitated on boiling. Various attempts were made to overcome this difficulty. It was noticed that the solution had a yellow color which disappeared on heating, and then the tin precipitated. It was thought that the color was due to the polysulphide, K_2S_x, and as long as it is present all the sulphur is in that form, but on heating the yellow colors disappears and the polysulphide is broken down. The free sulphur dissolves in hot KOH forming potassium thiosulphate.

$$6KOH + 4S = 2K_2S + K_2S_2O_3 + 3H_2O.$$

This hypo probably caused the precipitation of the tin and an attempt was made to prevent its formation. Alcohol seemed to prevent such a formation by forcing all the free sulphur into the polysulphide, and by the use of alcoholic potash a perfect separation was made.

The object of this work was to test the accuracy of the proposed method and to devise a new method for the further separation

of the tin and antimony.

The sulphides of tin (ic), arsenic and antimony dissolved readily in 1/2%, 1% and 2% solutions of KOH and alcoholic KOH, but on heating the solution of stannic sulphide tin was precipitated in each case. It was thought that if all the tin could be precipitated, and arsenic and antimony extracted with KOH it would be easy to separate the tin from the copper, lead and bismuth. An alloy containing copper, lead, antimony, tin, iron and zinc was dissolved in hydrochloric acid and a small amount of nitric acid, and oxidized with H_2O_2. The sulphides were precipitated with H_2S, filtered and washed. The mixed sulphides were boiled with 1/2%, 1% and 2% solutions of KOH and small amounts of KSO_4 added. In each case tin was found in the filtrate and as the amount of KSO_4 was increased the copper dissolved. The KSO_4 reacts with the KOH according to the equation:

$$2KOH + 2KSO_4 = 2K_2SO_4 + H_2O + O.$$

The sulphides were boiled with a 1% solution of KOH and the equivalent of KSO_4 was added. The solution was neutral, contained all the copper and no tin but considerable difficulty was found in washing out the copper from the undissolved sulphides. Tests made on the sulphides of tin and antimony with KOH and KSO_4 showed that the tin was not all precipitated until the neutral point was reached, and at that point the antimony begins to come down. By adding a few cc. of an ammonium acetate solution all the tin is precipitated when the neutral point is reached and the antimony does not precipitate when more KSO_4 is added. Here then would have been a new method if the difficulty of washing out the copper could be overcome.

The equivalent of KSO_4 was next dissolved in the cold in a solution of KOH, and this mixture added to the mixed sulphides and boiled. The filtrate contained antimony and tin but no copper or lead. The presence of tin, may have been due to an insufficient amount of KSO_4 and although no tests were made it seems possible that by the addition of a few c.c. of ammonium acetate solution and a greater amount than the equivalent of KSO_4, a complete separation might be made.

An attempt was made to prevent the precipitation of the tin by adding the KOH to the sulphides in small portions and boiling the mixture after each addition. Stannic sulphide was suspended in water and a 1% solution of KOH added from a burrette in portions of two or three cubic centimeters. The solution was boiled after each addition of KOH, and tested from time to time with litmus paper. When the solution remained faintly alkaline after boiling for a few minutes, all the tin sulphide had dissolved and the solution remained clear upon further boiling. Tests were made upon different amounts of stannic sulphide in order to find how large an excess of KOH could be added without precipitating the tin on boiling, and it was found that the addition of four times as much more as was required for alkalinity would not precipitate the tin.

This method was then tried upon the mixed sulphides precipitated from a solution of an alloy, and it was found that all the tin and antimony was extracted. The alloy is dissolved by boiling with conc. HCl (Sp. gr. 1.12) and adding a few drops of nitric acid to aid solution. The danger of volatilizing the chlorides of antimony and tin by boiling, may be avoided by using conc. HCl (Sp. gr. 1.20) which requires less heat to bring about the

solution. The addition of tartaric acid prevents the precipitation of the oxy-chloride of antimony on dilution. The solution is diluted to several times its volume with water and the sulphides precipitated with H_2S. After passing H_2S into the solution for several minutes the solution is further diluted until the volume is from twenty to twenty-five times its original volume. These were found to be the conditions for the complete precipitation of the sulphides. The solution was filtered hot and thoroughly washed with hot water. The filtration on asbestos was more rapid but the complete removal of the sulphides from the sides of the funnel was difficult. The filter paper containing the mixed sulphides is thrown into water and a 1% solution of KOH added in small portions. The solution is boiled after each addition of KOH and when the point of alkalinity is reached, four times as much more KOH is added in larger portions than before. Ten to twenty cc. of H_2O_2 made slightly alkaline with KOH are added and the solution boiled and filtered. Although a complete extraction was obtained, a more certain way would be to make two extractions using one-half as much KOH for each. The residue is treated with concentrated nitric acid, filtered on asbestos, and the lead, copper and bismuth separated and determined in the usual way. A few cc. of ammonium acetate are added to the filtrate and the solution is boiled. KSO_4 is now added in small amounts until the solution is slightly acid.

$$K_2SnO_3 + 2KSO_4 = 2K_2SO_4 + SnO_2 + O.$$

the solution is filtered and the residue, SnO_2, ignited and weighed.

The alloys used contained only tin and antimony and the filtrate, therefore, contained only antimony. Oxalic acid is added in considerable excess and the antimony precipitated with H_2S,

filtered, and washed. The precipitated sulphide is then washed from the filter paper, the solution brought to dryness, and treated with fuming nitric acid until all the free sulphur was oxidized. The antimony oxide, Sb_2O_3, is then filtered on a weighed platinum Gooch crucible, ignited and weighed. If arsenic is present the filtrate from the tin is made alkaline with ammonia and the arsenic precipitated with magnesia mixture. The filtrate from the arsenic is made acid again and the antimony precipitated as above.

TABLE OF ANALYSIS OF TIN AND COPPER GROUP.

0.2 gr. alloy dissolved in HCl (Sp. gr. 1.20) and a little HNO_3.
Solution oxidized with 10 cc. H_2O_2 - Tartaric acid added.
Dilute to several times original volume.
Pass H_2S - dilute to 20 - 25 times original volume.
Pass H_2S - filter.

Residue Pb Cu Sn As Sb.
Digest with 1% KOH added from a burrette in portions of 2 or 3 cc. until alkaline. Boil after each addition.
Add four times as much more KOH.
Add 10 cc. H_2O_2 boil - filter - wash.

Filtrate Zn. Fe. Al. Separate by usual method.

Residue Cu Pb.
Dissolve in HNO_3.
Add H_2SO_4 conc.
Boil to SO_3 fumes.
Dilute, add equal volume alcohol, filter on weighed Gooch crucible.

Filtrate Sn. As. Sb.
Add ammonium acetate solution.
Add KSO_4 until acid.
Filter - wash.

Residue $PbSO_4$.
Dry - ignite, weigh.

Pb.

Filtrate Cu.
Determine by Parr method.

Cu.

Residue SnO_2.
Ignite, weigh.

Sn.

Filtrate As Sb.
Make solution alkaline.
Add Mg mixture.
Filter - wash.

Residue $MgNH_4AsO_4$.
Ignite, weigh as $Mg_2As_2O_7$.

As.

Filtrate Sb.
Make acid.
Pass H_2S.
Filter - wash.
Residue Sb_2S_3.
Treat with fum. HNO_3.
Filter on weighed Gooch.
Ignite, weigh as Sb_2O_3. Sb.

QUANTITATIVE WORK.

The method above was used for all the determinations and in some cases two extractions were made with KOH.

Brass Boxing Ill. Cent. No. 2.

6.51% tin

6.59% tin

6.42% tin

6.51% tin

Complete analysis Brass Boxing Ill. Cent. No. 2.

tin	6.51%	6.59%
lead	13.86%	13.80%
copper	70.65%	70.68%
iron	.60%	.60%
zinc	8.40%	8.47%
total	100.02%	100.14%

Babbitt No. 1. R.I. Plow Co.

8.18%	tin	10.65%	antimony
8.18%	tin	11.25%	antimony
8.07%	tin	14.80%	antimony
8.10%	tin	14.74%	antimony
8.18%	tin		
8.21%	tin		

The first two results on antimony were probably low because only one extraction was made with KOH.

REFERENCES.

(1) Zeitschrift fur analytische Chemie, Vol. 27, 1888, p. 218.

(2) Zeitschrift fur Analytische Chemie, Vol. 27, 1888, p. 651.

(3) Journal of the American Chemical Society, Vol. 7, 1885, p. 133.

(4) Annalen der Chemie, Vol. 192, p. 317.

(5) Zeitschrift fur Analytische Chemie, Vol. 34, 1895, p. 596.

(6) The Analyst, Vol. 20, 1895, p. 46.

(7) Chemical News, Vol. 57, 1888, p. 125.

(8) Zeitschrift fur Analytische Chemie, Vol. 39, 1900, p. 47.

(9) School of Mines Quarterly, Vol. XXIV, No. 1, Nov. 1902, p. 90.

(10) Chemical News, Vol. 45, 1882, p. 101.

(11) Chemical News, Vol. 46, 1882, p. 285.

(12) Chemical News, Vol. 77, 1898, p. 36.

(13) Chem. Central - Blatt, Vol. 73, 1902, p. 67.

(14) Chem. News, Vol. 46, 1882, p. 172.

(15) The Analyst, Vol. 27, 1902, p. 99.

(16) Journal of the American Chemical Society, Vol. 19, 1897, p. 935.

(17) Zeit fur Analytische Chemie, Vol. 34, 1895, p. 596.

(18) Journal Society of Chemical Industry, Jan. 15, 1902.

(19) Journal Society of Chemical Industry, May 31, 1901.

(20) Thesis University of Illinois, 1902.

UNIVERSITY OF ILLINOIS-URBANA
3 0112 086855514